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Poly(aryline imides) as E-Beam Resist: Sensitivity and Resolution

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Synopsia

Polyamic acids synthesized from di-trifluoromethyl methane bis(phthalic anhydride) and 4,4'-diaminophyenyl sulfone (F-1) and 4,4'-diaminophenyl ether (F-4) were found to have excellent negative E-beam resist properties. The best materials contain about 90% imidized structural units having sensitivities of 1.5 to 2.5 pc/cm and contrast of 1.0 to 1.3. Polyamic acid of pyromellitic dianhydride and 4,4'-diaminophenyl sulfone (P-1) imidized to 97% exhibits useful positive E-beam resist properties. Radiation induces imidization and chain scission to alter the solubility of the resist polymers resulting in the formation of latent images. Imides any radicals.

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INTRODUCTION

Polymeric materials are used in conjuction with the technology of VLSI in two main areas. The first is the E-beam resist applications. Several monographs are now available on the subject. In our laboratory, we have investigated the halogen atom sensitization effect¹⁻⁵ and low ceiling temperature polymers^{6,7} in E-beam lithography especially concerning the possibility of self-developing direct imaging positive resists.

Thermally stable polymers found the following usages in VLSI: (1) passivating overcoat, (2) interlevel dielectrics, (3) multi-level multi-conductor substrates, (4) adhesive for bonding a substrate to the chip^{e-10}. Polyimides are the preferred materials in these applications.

There have been proposals to use polyimides in photoimaging systems. 11.12 So far, photo-active ingredients are
needed which are not heat stable. The photosensitizers
need to be decomposed and volatilized; their complete
elimination had been one of the technical difficulties. The
other shortcomings are the limited shelf-life stability and
shrinkage in curing resulting in image distortion and stress
build-up.

The central purpose of this work is to discover a polyimide resist system which does not need a sensitizing additive and forms high resolution image without shrinkage. The preparation of the polyimide resists and their radiolytic behaviors are given in the accompanying paper.13

polyimide resists and their radiolytic behaviors are given in the accompanying paper.13

EXPERIMENTAL

Materials

The synthesis of polyamic acids are given in detail elsewhere¹³; their structures are given below:

F-1
$$\left\{N, \frac{0}{6}, \frac{c_{F_3}}{c_{F_3}}, \frac{0}{6}, N - 0 - so_2 - 0\right\}$$

$$F^{-3} = \left\{ \begin{array}{c} 0 & C_{F_{3}} & C_{F_{3$$

$$F-4 = \left\{ \begin{array}{c} N < \begin{cases} 2 & CF_3 \\ CF_3 & C \\$$

The F series polymers were prepared from di-trifluoromethyl methane bis(phthalic anhydride) (F6 dianhydride) and the P series polymers were prepared from pyromellitic dianhydride. Imidization

Imidization was carried out in a thermal reactor under an atmosphere of nitrogen monitored by 1380 cm⁻¹ and 1780 cm⁻¹ band intensities for the C-N and C=O vibrations respectively. The degree of imidization (D.I.), is estimated from the ratio of optical density at 1380 cm⁻¹ following heat treatment to the optional density after 15 min. of heating at 300°C, the latter corresponds to complete imidization. Figure 1 shows the IR spectral changes with imidization; figure 2 plots the degree of imidization versus temperature of heating for 5 min.

Polyimide samples with various degree of imidization were prepared as described in Table I.

Gamma irradiation

Gamma irradiation was performed with a ¹³⁷Cs source and the dose rate determined by Fricke dosimetry.

E-beam lithography

Polymer was dissolved in dimethyl formamide (10% in DMF) and the solution spin-coated on a silicon waffle and prebaked for 10 min. at 120°C. The resist film, about one micron thick, was exposed to a 20 keV electron beam with a JEOL JSM-35 CF scanning electron microscope, and the image

polyamic acid	170°C	Degree of	imidiza	286°C	300°C
F-1	38	73	91	98	- 100
F-2	45	80	96	98	~ 100
F-3	54	79	90	97	-100
F-4	62	81	90	96	~100
P-1	41	69	87	97	-100
P-2	66	72	90	96	~100
P-3	33	65	89	98	-100
P-4	68	75	91	98	-100

After 5 min. of heating at indicated temperatures except it was >15 min at 300°C to affect complete imidization.

developed with a <u>i</u>-propanol/DMF mixture for 2 min. and rinsed with <u>i</u>-propanol. The thickness of resist was measured with interference microscopy.

RESULTS AND DISCUSSION

F-1 and F-4 were found to be excellent negative resists; these performances vary with D.I. Figure 3 gives the variation of thickness with dose. From these curves the values of sensitivity and contrast, y were calculated (Table II). Figure 4 and Table III contain the results for F-4.

Neither the polyamic acid nor the polyimide of either polymer acts as resist but the copolymer does. The structure of the random copolymer may be represented by

Table IV summarized the results of these and other polymers.

The best performing polymers have D.I. between 90-97%.

Figure 5 is a plot of sensitivity versus D.I. for F-1 and F-4. F-3 and P-3 are useless as resists because they are

Table II. Properties of F-1 polyimides in E-beam lithography

D.I.,%	Developer DMF: <u>i</u> -propanol volume ratio	Sensitivity µ C cm ⁻²	Υ	Resolution
0	1:20	-	_	poor
38	1:4	10	-	poor
73	1:3	5	1.2	good
91	3:4	2.5	1.1	excellent
98	1.1	3 .	1.0	excellent

Table III. Properties of F-4 polyimides in E-beam lithography

D.I.,%	Developer DMF: <u>i</u> -propanol volume ratio	Sensitivity µ C cm ⁻²	Y	Resolution
0	1:20	-	-	poor
62	1:3	8.0	0.96	good
81	1:2.5	4.5	0.89	good
90	1:1	1.5	1.3	excellent
96	1:0.5	2.0	1.1	poor

insoluble at any D.I.

P-1 is the only material which acts in the positive mode to E-beam irradiation. Figure 6 and Table V give the detail results.

Table IV Summary of E-beam lithographic properties

Sample	D.I.,%	Developer DMF: <u>i</u> -propanol	Sensi- tivity µ C cm-	Resolution a	Mode	Usefulness
F-1	91	3:4	2.5	excellent	neg.	excellent
F-2	96	2:1	6.5	excellent	neg.	excellent
F-4	90	1:1	1.5	excellent	neg.	excellent
P-1	97	1:0	8	good	pos.	useful
P-2	90	1:0	8	good	neg.	poor
P-4	75	1:0	~	poor	neg.	useless

The excellent negative E-beam resist properties found for the F-series polyimides and and their dependence on D.I. are both unexpected. The polymers were synthesized with the hope that they will be good positive E-beam resist based on

Table V Properties of P-1 polyimides in E-beam lithography

D.I.,%	Developer DMF: i-propanol volume ratio	Sensitivity, µC cm ⁻²	Y	Resolution
0	0:1	<u>-</u>	-	_
41	1:3	-	-	-
69	1:2	_	-	-
87	2:1	7	0.9	good
97	1:0	8	1.0	good
-100	1:0	10	1.7	good

the sensitivity of sulphone moiety to energetic radiation. 15-17 Alternating copolymers of olefin and SO₂, poly(alkylene sulfones), have G-values of up to twenty SO₂ and olefins produced per 100 eV. It was reported in the accompanying paper 13 that the F-series polyimides has G_S values between one and two scissions per 100 eV. These G_S values are comparable to that for poly(methyl methacylate) which is a commercially used E-beam positive resist.

Therefore, some other mechanism is responsible for the negative E-beam resist action of the F-series polyimides.

Sample of F-1 with 73% D.I. was irradiated with yradiation for five days. Infrared spectra (Figure 7a)
showed that the D.I. was raised to 88%. Similarly, an F-1
sample with 91% D.I. was irradiated, the D.I. increased to
99% after 5 days of irradiation (Figure 7b). Since the
solubility of the polymer decreased with the increase of
D.I., the exposed region has lowered solubility. In this
way, this discovery of negetive E-beam resist properties for
the F-series polyimides and their dependence on D.I. can be
explained. The superior properties of the F-series than the
P-series may be simply because the former have better
solubility characteristics. The positive E-beam behavior of
the P-1 material is different from the F-series but is along
the line of our initial expectation.

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